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Far-Infrared Spectroscopy of Nucleic Acids

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ABSTRACT: Hydrogen bonding interactions are crucial to the stabilization of the DNA double helix. The effects of periodic hydrogen bond pattern in repeat sequences are likely to give rise to defined low frequency modes in oligonucleotide models. Despite the great interest in the structure and dynamics of polynucleotides, very little spectroscopic work has been done in the far-infrared region. The far-infrared is a region of the spectrum in which low frequency vibrational motions are found, for example: hydrogen bonding and large dynamical molecular motions. Thus, far-infrared spectroscopy provides a method for the investigation of the hydrogen-bonding environment of a molecular system. Moreover, the temperature dependence of low frequency modes reveals their anharmonic coupling. As the temperature is lowered, the ground state population increases relative to all excited states. For an anharmonic transition, the energy gap between any two successive vibrational states gets smaller as the vibrational quantum state increases. That is, as the population of the ground state increases the frequency of the vibrational transition increases. We use the temperature dependence as evidence for anharmonic coupling.

The temperature dependent far-infrared analysis of purine nucleic acid components has been conducted at the NSLS U2B beam line. Specifically polycrystalline adenine and 2-deoxyadenosine and their isotopically labeled analogs, adenine was singly labeled with ^{13}C at positions C(2) & C(8), with ^{15}N at exocyclic amino (N(6)) & N(9), and triply labeled with ^{13}C at C(8) and ^{15}N at N(6) & N(9). Isotopic 2-deoxyadenosine was singly labeled with ^{15}N at exocyclic amino (N(6)) & N(9), doubly labeled with ^{13}C at C(8) and ^{15}N at N(9), and triply labeled with ^{13}C at C(8) and ^{15}N at N(6) & N(9). Deuterated derivatives of adenine, 2-deoxyadenosine and their isotopomers were prepared by way of hydrogen exchange reflux, for a minimum of 4 hours, at 40°C in D_2O . De-ionized 18M Ω water exchange was also performed on both the natural abundance and the isotopic compounds as a control.

These investigations focused on the experimental determination of the effects that isotopic labeling has on the low frequency vibrational modes of these important biochemical compounds. The fact that so many low frequency modes appear to have strong temperature dependence is something of a surprise. Given the studies of anharmonic coupling in other biological molecules (e.g. the axial vibrations of the heme iron in heme proteins) one might have expected only one or two of the modes to show significant anharmonic coupling with the remaining modes displaying mode "harding" (i.e. normal coordinate frequency shift that results from bond contraction). The fact that so many modes show a large temperature dependence (i.e. anharmonic coupling as opposed to "mode harding") has slowed efforts to identify relationships that are unique to the hydrogen bonding interaction. The goal of future studies is to obtain similar data in oligonucleotides in crystalline and glassy forms in order to determine the effect of hydrogen bond patterns on vibrational spectra in the far-infrared region.